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Organic-Template-Directed Nucleation of Strontium Fluoride and Barium Fluoride

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Beamline(s): X14A

Introduction: Langmuir monolayers are often used as templates for nucleation of inorganic compounds; they exert profound control over the size, structure, morphology and orientation of inorganic crystals [1]. Such control is possible because, as we have recently observed with barium fluoride [2], the unit cell of the salt contracts at the fatty-acid template at an early stage of growth. In this study, we analyze the broadening of diffraction peaks of barium fluoride to obtain information on the domain size and the extent of crystal defects during the initial stage of growth. We also test whether the organic monolayer has a similar effect on strontium fluoride. We expect to see the same relaxation in strontium fluoride because it is isostructural with barium fluoride.

Methods and Materials: Supersaturated aqueous solutions of strontium fluoride were prepared at concentrations of 4.5mM and 7.5mM by mixing appropriate stoichiometric amounts of strontium chloride and ammonium fluoride. (Sigma, quoted purity 99.99%). The pH was adjusted with sodium hydroxide (Sigma, quoted purity 99.998%) to 8.0 and measured in the beaker before the solution were poured into the trough. About 65 μL of a 0.87 mg/mL solution of heneicosanoic acid ($C_{20}H_{41}COOH$, or C_{21}, Sigma, quoted purity 99%) in chloroform was spread on pure on the aqueous solutions.

Results: The integral breadth of diffraction lines depends on the Bragg angle (not shown); from that, it follows that both size and strain effects must be contributing to the broadening of the peaks. We fit the trend using methods of integral breadths [3] and extract the in-plane size of domains, *L*, and the maximum non-uniform strain, *e,* as parameters of the fit. The domain size is about 200Å at low concentrations, and as the crystallites grow at higher concentrations, the length of the domain size increases up to about 500Å as shown in Fig 1b. Peaks at all concentrations are broader than the resolution limit of about 1000Å.

The non-uniform strain (microstrain) decreases as the domain size increases and as the peak positions approach their ideal, bulk values. At the lowest concentration, when the domain size is small, the maximum non-uniform lattice distortion is about 0.004 and drops off only slightly with increasing concentration as shown in Fig 1a. This trend is consistent with the expectation that the structure takes on its usual, non-strained form as crystallites grow.

We find that peaks of strontium fluoride, like those of barium fluoride, 'shift' in the reciprocal space; the unit cell is contracted by 1.6% from the bulk value of 5.8 Å at the onset of growth (Fig. 2). In contrast to those of barium fluoride, peaks of strontium fluoride shift quickly with time. The intensity variations along the curves on Debye rings (Fig. 3) indicate that strontium fluoride also grows preferentially oriented with its <100> face to the fatty-acid template. The extent of misorientation is only ±5º FWHM at 7.5 mM.

Conclusions: Our experiment with strontium fluoride shows that just as with barium fluoride, the crystallographic structure of the salt is not rigid in the initial stage of growth. Although the organic matrix is destroyed too early to observe epitaxy, we suspect that as in the case of barium fluoride, it is this structural flexibility of strontium fluoride what allows the salt to grow preferentially oriented at the fatty-acid template. The peak shifting is correlated with strong broadening effects from metastable supersaturated solutions of barium fluoride and can be attributed to microstrain, which is associated with the concentration of the dissolved compound. The structural defects in the initial stage is what accounts for the flexibility of the inorganic lattice at the early stage of nucleation and allows atomistic ordering of inorganic atoms at the structured organic interface.

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References: [1] Mann, S., Nature, **365**, *499-505* (1993); [2] Kmetko, J., Yu, C.-J., Evmenenko, G., Kewalramani, S., and Dutta P., Phys. Rev. Lett. **89**, *186102* (2002); [3] Klug, H. P., Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley: New York, 1974.

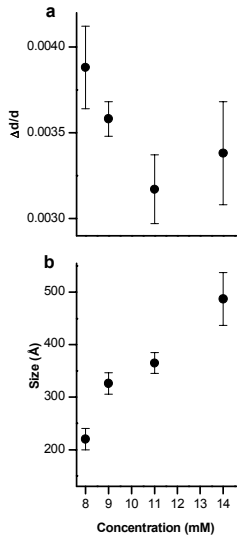

Figure 1: Microstrain relaxation in barium fluoride at the mineral-matrix interface. The microstrain in (a) and the domain size in (b) have been determined from fits to the line shapes.

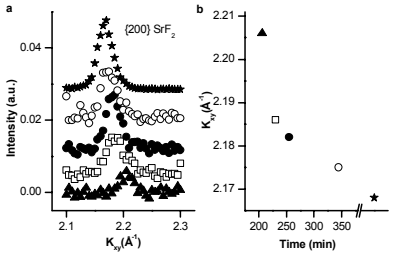

Figure 2: Macrostrain relaxation in strontium fluoride at the mineral-matrix interface. (a) A representative {200} diffraction peak 'shifts' as a function of time at concentration of 4.5mM. The following symbols denote time after spreading the organic film (in minutes): 7 206, ∀ 230, , 255, – 345. The peak from a slightly more concentrated solution (7.5mM) denoted by 'ξ' appears at the ideal, bulk position. (b) The mineral begins to grow strained by as much as 1.6% from its bulk structure.

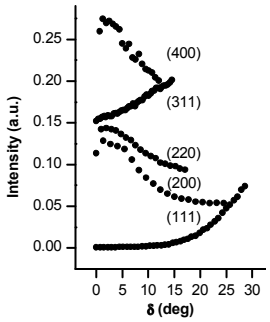

Figure 3: At high supersaturation, the diffracted intensity is entirely peaked along the Debye rings. The maxima of the intensity distribution indicate that the crystallites are preferentially oriented with the <100> face parallel to the plane of the water surface. The angle δ is defined as $\tan\delta = |K_z| / |K_{xy}|$; the total wave vector $K = \sqrt{K_{xy}^2 + K_z^2}$ is the 'radius' of the Debye ring. Intensity values for data points of the (111) curve have been divided by 50 and for the (200) and (311) curve by 5 so that they can be shown on the same scale.